

Ferroelectricity in ultrathin film capacitors

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Contents

1	Introduction	2
2	Ferroelectricity. Basic definitions	3
3	Theoretical methods for the study of bulk ferroelectric materials	6
3.1	Devonshire-Ginzburg-Landau (DGL) phenomenological theory	6
3.2	First-principles simulations	7
3.3	Second-principles methods: model Hamiltonians and shell models	8
4	Modeling ferroelectricity in oxides	9
5	Theory of ferroelectric thin films	13
5.1	Mechanical boundary conditions: strain	14
5.2	Electrical boundary conditions: imperfect screening	16
5.3	Electrical functionals with a depolarization field	20
5.4	Chemical-bonding contributions to the electrical boundary conditions	21
6	Polarization domains and domain walls	22
6.1	Kittel law	22
6.2	Domains morphology	23
6.3	Domain walls	25
7	Artificially layered ferroelectrics	26
7.1	Electrostatic coupling	26
7.2	Engineering ferroelectricity at interfaces	28
8	Conclusion and perspectives	30

1 Introduction

Ninety years ago Valasek discovered that the permanent polarization of Rochelle salt could be reversed with an applied electric field, giving rise to a hysteretic polarization-field response [208, 207]. By analogy with ferromagnets, such materials became known as ferroelectrics, and have since attracted considerable interest from a fundamental aspect and because of their wide range of potential applications. Ferroelectric materials are also *piezoelectric*, i.e. electric charges appear at their surface (due to changes in polarization) when they are under mechanical strain, and vice versa, as well as *pyroelectric*, i.e. their electrical dipole moment depends on the temperature. These properties find many applications and make these materials technologically important. Thermal infrared pyroelectric detectors, ultrasound transducers, non-volatile ferroelectric Random Access Memories (FeRAM) [165] for smart cards and portable electronic devices, surface acoustic wave devices for filters in telecommunications and gravimetric sensors, membrane type actuators useful in micropump devices, ultrasonic micromotors, ultrasonic transducers and sensors for medical imaging,

and other medical applications for blood pressure control are just a few examples of the many technological applications using these materials. Going down to the limit of ultrathin films holds promise for a new generation of devices such as ferroelectric tunnel junctions [204, 108, 44, 43] or resistive memories [81]. However, these length scales also make the devices sensitive to parasitic effects related to miniaturization, and a better understanding of what happens as size is reduced is of practical importance for the future development of these devices. This chapter is about what happens to ferroelectric films as we go nano.

This is a particularly exciting time for nanoscale physics, as the experimental advances in materials preparation and characterization have come together with great progress in theoretical modeling of ferroelectrics, and both theorists and experimentalists can finally probe the same length and time scales. This allows realtime feedback between theory and experiment, with new discoveries now routinely made both in the laboratory and on the computer. Throughout this chapter, we will highlight the recent advances in density functional theory based modeling and the role it played in our understanding of ultrathin ferroelectrics. We will begin with a brief introduction to ferroelectricity and ferroelectric oxides in section 2, followed by an overview of the major theoretical developments in section 3. We will then discuss some of the subtleties of ferroelectricity in perovskite oxides in section 4, before turning our attention to the main subject of the chapter – ferroelectricity in ultrathin films in section 5. In this section we will discuss in detail the influence of the mechanical, electrical and chemical boundary conditions on the stability of the polar state in a parallel plate capacitor geometry, introducing the notion of depolarization fields that tend to destabilize ferroelectricity. In section 6, we will look at other ways in which a thin ferroelectric can preserve its polar state, focusing on ferroelectric domains and domain walls. Finally, in section 7 we will briefly discuss artificially layered ferroelectrics and the potential they hold as tailor-made materials for electronic applications.

Of course, it is impossible to summarize 90 years of research within the scope of this chapter. We will only review some of the stimulating developments that took place in the field of ferroelectric thin films within the last few years and will point the attention of the interested reader to the most comprehensive books and reviews summarizing the state of the art of this exciting field of research, both theoretically and experimentally.

2 Ferroelectricity. Basic definitions

Ferroelectrics are materials exhibiting a spontaneous electric polarization that can be switched by applying an electric field. The value of the spontaneous polarization can vary over several orders of magnitude depending on the material (see Fig 1 (a)). The word “ferroelectric” is actually somewhat of a misnomer as these materials rarely contain iron. The prefix “ferro” was instead adopted by analogy with the more mature field of ferromagnetism, which has many parallels with ferroelectricity: (i) a ferromagnet has a *spontaneous magnetization* that can be switched by an external magnetic field, (ii) the switching process can be associated in both cases with an hysteresis loop [see Fig. 1 (b)], (iii) very often there is a coupling between polarization (either magnetic or electric) and the shape of the unit cell (strain), (iv) both the ferroelectric and ferro-

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magnetic polarization decrease with increasing temperature up to a critical T_c , where a phase transition to a high-symmetry unpolarized phase takes place and the corresponding polarization order parameter vanishes, and (v) even below T_c the macroscopic polarization might vanish if the homogeneously polarized state breaks into *domains* (regions with oppositely oriented polarization within the sample). Despite all these similarities, one must keep in mind that the microscopic origin of these two phenomena are different, so a direct extrapolation from one world into the other is not always possible. As an example, the domain walls in ferromagnets are orders of magnitude wider than those in ferroelectrics. A complete side-by-side analysis of analogies and differences can be found in Ref. [181].

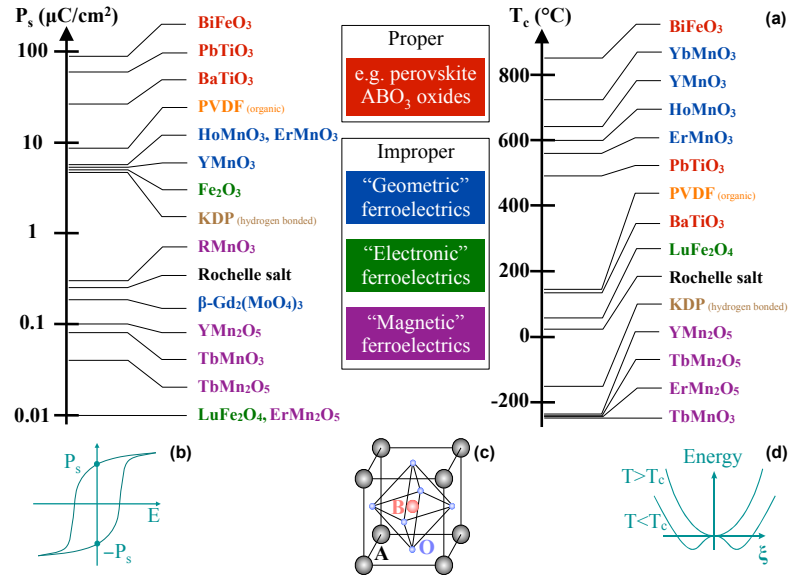


Figure 1: Ferroelectrics encompass an enormous range of compounds, with a multitude of structures and compositions, both organic and inorganic. (a) Their defining and technologically relevant properties – the spontaneous polarization (P_s) and the critical temperature (T_c) – cover a wide range of values. (b) Ferroelectric materials display an hysteresis loop between polarization and electric field. (c) Among proper ferroelectrics, perovskite oxides with the generic formula ABO_3 have received most attention due to their simple structure, chemical stability and large polarization values. The structure of the high-temperature paraelectric phase for most ferroelectric perovskite oxides is cubic, as the one shown schematically. (d) While hysteresis loops constitutes the measurement of choice to experimentally demonstrate ferroelectricity, the existence of a double-well energy landscape as a function of a macroscopic polar mode coordinate ξ is usually considered as the theoretical fingerprint of the ferroelectric instability.

When an electric field is applied to any *insulating* material, the bound electric charges inside the material will move on a short scale. The material becomes polarized. If the applied electric field E is not too large, then the polarization response of the dielectric P_d can be assumed to be linear,

Ferroelectricity in ultrathin film capacitors

$$\mathbf{P}_d(\mathbf{E}) = \varepsilon_0 \chi \mathbf{E}, \quad (1)$$

where ε_0 is the vacuum permittivity, and χ is the electric susceptibility tensor of the dielectric (throughout this chapter we will use the SI system of units). If the medium is isotropic the χ can be considered as a constant of proportionality independent of the direction.

In a ferroelectric material the symmetry is spontaneously broken so, even in the absence of an external electric field, there are two or more polar states with a non-vanishing spontaneous polarization, \mathbf{P}_s . If a *small* electric field is applied when the system is in one of these stable polarization states, the total polarization of the ferroelectric reads

$$\mathbf{P}_f(\mathbf{E}) = \mathbf{P}_s + \varepsilon_0 \chi \mathbf{E}. \quad (2)$$

However, having an spontaneous polarization is just one of the conditions for a material to be classified as ferroelectric. The second requirement is that it should be possible to switch from one polar state to another by applying a field that is larger than a threshold value, called the *coercive field*, \mathbf{E}_c . The switching mechanism typically proceeds via nucleation and growth of inverted domains [176], with an external electric field inducing the domain-wall motion; this leads to the modification of the domain volumes and thus of the total polarization. Nevertheless, this is an area of continuing interest and controversy and there exist exceptions to the above scenario. For example, a continuous switching mechanism without domain formation has been reported very recently for PbTiO_3 thin films; note that this behavior occurs only at certain values of thickness and temperature [61].

Ferroelectricity has been reported in different families of compounds, including hydrogen bonded systems (for a review see Ref. [85] and the special issue in Volume 71 of *Ferroelectrics* journal, 1987) such as KDP (potassium dihydrogen phosphate; KH_2PO_4), polymeric systems (review in Ref. [119]) such as PVDF (poly-vinylidene fluoride; $[-\text{CH}_2-\text{CF}_2-]_n$), or the wide family of ferroelectric *perovskites* ABO_3 , where A is a mono-, di- or tri-valent cation and B is a penta-, tetra- or tri-valent cation, respectively.

Perovskite ferroelectrics in particular have generated an enormous amount of interest, in part due to their simple structure, and will be the focus of this chapter. In most cases, this family of compounds crystallizes at high temperature in a simple cubic paraelectric phase with five atoms per unit cell ¹: the A cation at the corner of the cube, the B cation body-centered and the O anions face-centered, as represented in Fig. 1(c). This is known as the “ideal” perovskite structure and is typically taken as the high-symmetry reference configuration in theoretical studies. Its simple crystalline structure along with a large spontaneous polarization makes this family of compounds widely used in applications and as model systems for theoretical studies.

Below T_c , the system undergoes a structural phase transition, lowering the symmetry of the high-temperature paraelectric state. The unit cell becomes non-centrosymmetric, and can display several equivalent configurations. In the case of a tetragonal configuration, for example, there are two equivalent antiparallel polarization states along the polar c -axis. In a simplified model, the

¹ LiNbO_3 and related materials are exceptions, where the paraelectric phase has a rhombohedral unit cell with two formula units per unit cell.

phase transition can be characterized by the motion of the B-cations with respect to the O cage. This polar atomic distortion usually also induces a small deformation of the unit cell.

A more detailed introduction of the essential background on the physics of ferroelectrics can be found in the classical works of Lines and Glass [101], and Strukov and Levanyuk [193], while a more recent perspective is available in the first chapter of the book edited by Rabe, Ahn, and Triscone [145].

3 Theoretical methods for the study of bulk ferroelectric materials

3.1 Devonshire-Ginzburg-Landau (DGL) phenomenological theory

For many years, the method of choice for the theoretical study of ferroelectric materials has been the phenomenological approach based on the Ginzburg-Landau theory, first applied to the case of ferroelectrics by Devonshire [32, 33]. The starting point of this theoretical model of phase transitions is the identification of an *order parameter*: a physical quantity that is zero in the high-symmetry phase and changes to a finite value once the symmetry is lowered. In the case of ferroelectric materials at the paraelectric-ferroelectric transition, this might be the polarization \mathbf{P} or the electric displacement \mathbf{D} (as done in Chapter 3 of the classical work by Lines and Glass, Ref. [101]). The second issue to deal with is the identification of the other relevant degrees of freedom in the problem under consideration. Independent variables have to be chosen among the conjugate pairs temperature-entropy (T, S) and stress-strain (σ, η). The choice is guided by the parameters under control in a given experiment. Depending on the combination of the degrees of freedom, the corresponding thermodynamic potential is known under different names [Helmoltz free energy, Gibbs free energy (elastic or electric), etc., see Chapter 3 of Ref. [101]]. It is important to note here that there is no “best” thermodynamic potential but only the “most suitable” functional for a specified choice of the boundary conditions.

The central *Ansatz* of the Landau approach is that the free energy can be represented as a Taylor expansion of the order parameter and the dependent variables in the neighborhood of the transition point, where only symmetry-compatible terms are retained. To illustrate the form of this functional in the simplest possible scenario, we can write the free energy of the ferroelectric in terms of a single component of the polarization, ignoring the strain field and taking as zero the energy of the free unpolarized crystal,

$$\mathcal{F}(P) = \frac{1}{2}\alpha_2 P^2 + \frac{1}{4}\alpha_4 P^4 + \frac{1}{6}\alpha_6 P^6 + \dots \quad (3)$$

As previously mentioned, the coefficients of the expansion generally depend on temperature. However, for practical purposes, most of them are usually considered as constants. For instance, to deal with second order phase transitions, it is enough to consider the quadratic coefficient as T -dependent, while α_4 and α_6 are fixed to positive constant values. It is assumed that α_2 has a linear dependency of the form $\alpha_2 = \beta(T - T_c)$ with β a positive constant and T_c the temperature of the ferroelectric-to-paraelectric phase transition. For $T > T_c$

the quadratic term is positive and the thermodynamic functional is a single well with its minimum corresponding to the non-polar $\mathbf{P} = 0$ phase. For $T < T_c$ the quadratic coefficient is negative, and the thermodynamic potential displays the typical double well shape. There are two minima for $\mathbf{P} \neq 0$ [see Fig. 1(d)].

The coefficients of the expansion are fitted to the experiment, which is usually performed in a regime close to the phase transition (although lately some efforts to determine them from first-principles [65] and thermodynamic integrations [45] have been carried out). Finally, the state of the system at a given temperature is found by minimizing this free energy. We encourage the interested reader to pursue more on this subject in the primer by Chandra and Littlewood [21].

Despite the many virtues of DGL theory, we must nevertheless keep in mind its limits of validity: it is strictly a macroscopic approach and thus it cannot describe microscopic quantities such as atomic displacements. Therefore, it is expected to be valid only on length scales that are much larger than the lattice constant; some care has thus to be taken when extending DGL theory to the case of ultrathin films. In addition, this model is only as good as its input parameters are, and extrapolations to temperature and strain values that lie outside a neighborhood of the phase transition should again be done with caution.

3.2 First-principles simulations

As mentioned in the introduction, the last few years have witnessed a rapid evolution of the atomistic modeling of materials. Nowadays, it is possible to describe and predict very accurately the properties of ferroelectrics using methods directly based on the fundamental laws of quantum mechanics and electrostatics. Even if the study of complex systems requires some practical approximations, these methods are free of empirically adjustable parameters. For this reason, they are referred to as “first-principles” or “*ab initio*” techniques. Due to its accuracy and efficiency, density functional theory (DFT) has emerged as one of the most widespread methodological tools. A comprehensive overview of DFT, whose development earned W. Kohn his Nobel Prize in Chemistry in 1998, can be found in the excellent books by Richard M. Martin [110] or J. Kohanoff [80].

First-principles simulations could not be applied to the study of ferroelectric materials until the early nineties, due to the lack of a formal theory of the polarization in periodic solids. While the polarization can easily be expressed in terms of the charge distribution for molecules (finite systems), it cannot be obtained that way for crystals (infinite systems treated periodically). Indeed, the naive Clausius-Mossotti definition of the polarization as a dipole moment per unit volume cannot be used, as it depends on the (arbitrary) choice of the unit cell [109]. The solution to this long-standing problem appeared in the early 1990s, and is often referred to as the “modern theory of polarization” [76]. The basic idea is to consider the change in polarization [149] of a crystal as it undergoes some slow change, e.g. a displacement of one sublattice relative to the others, and relate it to the *current* that flows through the crystal during this adiabatic evolution of the system [150]. A review on the modern approach to the theory of polarization can be found in Refs. [154, 152]. Once the access to the polarization of a periodic solid is granted, we can compute relevant quantities of interest such as the Born effective charge defined in Eq. (5), which are central

to the phenomenon of ferroelectricity as will be explained in Sec. 4.

After the establishment of the modern theory of polarization, a number of further methodological developments were proposed that significantly enhanced the capabilities of first-principles simulations of ferroelectric systems by allowing full control over the macroscopic electrical variables in periodic insulators. At the core of all these advances lies the method to introduce a finite macroscopic electric field in a periodic quantum-mechanical simulation [180, 205]. Based on this method, rigorous strategies to perform calculations at a specified value of \mathbf{P} [36] or, later, of the electric displacement \mathbf{D} [187] were subsequently established. These latter techniques opened the way to a direct computation of the “electrical equation of state” (energy as a function of \mathbf{P} or \mathbf{D}) of a bulk ferroelectric material from first principles. This has several advantages, that we summarize hereafter.

First, performing calculations at specified \mathbf{P} or \mathbf{D} bears a direct relationship to DGL theories, where \mathbf{P} or \mathbf{D} are commonly used as independent electrical variable. Second, the strength of the polar instability can be directly quantified by means of a generalized *inverse permittivity*, that is the second derivative of the total energy with respect to \mathbf{D} . This is an interesting alternative to the previously available estimates in terms of the imaginary frequencies of the soft mode. Third, by mapping the ground-state properties as a function of \mathbf{D} (or \mathbf{P}) one can very easily access all response properties of the system (e.g. dielectric, piezoelectric, etc.) in a non-perturbative way (i.e. non-linear at any order); this might be cumbersome or impossible to obtain within the standard linear-response technique. There are further advantages related to the use of \mathbf{D} as fundamental electrical variables in the calculations of capacitors or superlattice geometries; we shall review those later in the appropriate context.

First-principles methods generate a wealth of microscopic information, reproducing the various ground state structures and functional properties of ferroelectric materials. The price to pay for this is its computational costs that thwarts their use in systems larger than a few hundreds of atoms or in molecular dynamics simulations beyond a few tens of picoseconds.

3.3 Second-principles methods: model Hamiltonians and shell models

In order to extend the range of applicability of first-principles simulations to larger systems and time scales, and provide access to finite-temperature thermodynamic properties, many efforts have been devoted to the development of methods that capture the essential physics with few parameters that can be directly extracted from DFT calculations. Among these “second-principles” methods, the most widespread ones are the model Hamiltonians and the shell models.

The *model (or effective) Hamiltonian* is a microscopic approach based on (i) the identification of the most important degrees of freedom for describing the transition through the local mode approximation of Lines [100], and (ii) to perform a low-order expansion of the energy in terms of these degrees of freedom, with coefficients directly determined from total energy DFT calculations. In the 1990’s this model was successfully generalized to ferroelectric perovskite oxides [225, 226]. In simple ferroelectrics, the first step greatly reduces the number of relevant degrees of freedom. For instance, in the prototype BaTiO_3

ferroelectric oxide, the structural distortion nearly exactly corresponds to the freezing into the structure of one of the transverse optic modes at the Γ point, usually referred to as the *soft-mode*, and to a subsequent strain relaxation. A reasonable approximation for the study of the phase transition is therefore to only consider explicitly (i) the ionic degree of freedom of the soft-mode by means of a local mode (i.e. a local cooperative pattern of atomic displacement) ξ_i that will be associated to each unit cell i and (ii) the strains (homogeneous or inhomogeneous). As the amplitude of the ferroelectric distortion is relatively small, the Hamiltonian can then be written as a Taylor expansion in terms of ξ_i and strains limited to low orders (again, only the symmetry-allowed terms are kept). Once the expression for the model Hamiltonian is known, and the parameters have been fitted, one can very efficiently predict the value of the energy for arbitrary configurations of the local cooperative patterns ξ_i . The sampling of the parameter space can be performed via classical Monte-Carlo or Molecular Dynamic simulations to investigate the temperature behaviour of ferroelectrics. The standard output provides the mean values $\langle \xi \rangle$ and $\langle \eta \rangle$ (where η stands for the homogeneous strain) in terms of temperature, external pressure and electric field. The macroscopic polarization of the crystal $\langle \mathbf{P} \rangle$ is also readily accessible since the local polarization \mathbf{P}_i is directly proportional to the amplitude of the local mode ξ_i ,

$$\mathbf{P}_i = \frac{1}{\Omega_0} \bar{Z}^* \xi_i, \quad (4)$$

where \bar{Z}^* is the Born effective charge of the local mode as defined later in Eq. 5, and Ω_0 the unit cell volume.

A step by step explanation about how to develop a model Hamiltonian can be found directly in the original paper by Zhong and coworkers [226].

Within the *shell model* a given ion of static charge Z is modeled as a massive core, of mass m and charge X , linked to a massless shell of charge $Y = Z - X$. The core and the electronic shell within an ion are connected through a spring of force constant k . This core-shell interaction might be considered anisotropic and anharmonic (containing up to fourth order terms) for the O^{2-} ions to emphasize the large anisotropic polarization effects at the oxygens associated with the ferroelectric distortions. In addition to the Coulombic interaction, the model contains pairwise short range potentials accounting for the effect of the exchange repulsion between atoms. All these material-specific parameters are determined by first-principles calculations. Then, the equations of motion are solved for all these coupled springs. A complete description of the method is available in Ref. [168]. This methodology is able to describe very well the phase behaviour and ferroelectric properties of KNbO_3 [170], PbTiO_3 (with surface effects [171], and the coupling with the substrate [172] or depolarization fields [184]), BaTiO_3 and SrTiO_3 [203], including its solid solutions and ultrathin films [202].

As a summary of this Section, we schematically represent in Fig. 2 the length and time scales accessible within the different methodologies discussed before.

4 Modeling ferroelectricity in oxides

Since the early 1990s, many density-functional theory calculations were carried out, as a complement to the experiment, in order to understand the micro-

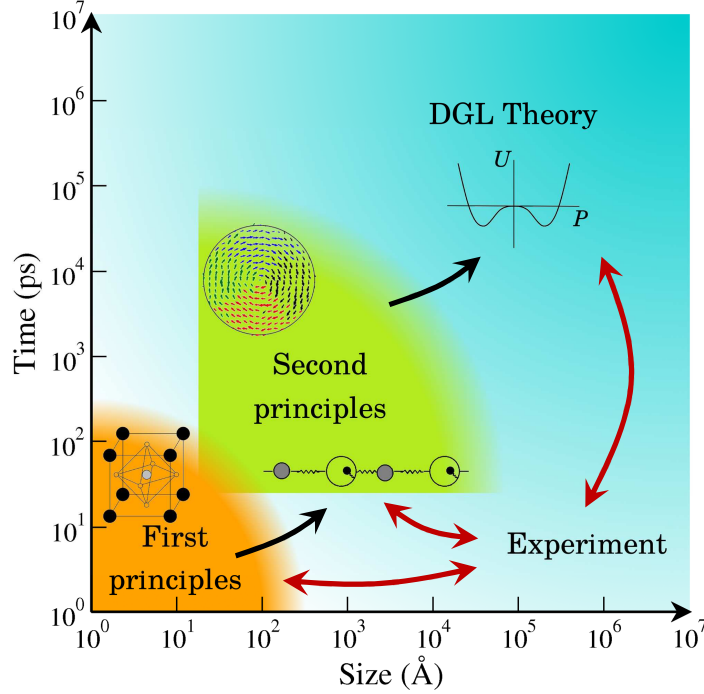


Figure 2: Sketch with the different length and time scales accessible with the various theoretical schemes presented in this chapter. Black arrows indicate the interconnection of the methods. First-principles methods with atomic resolution (represented by the balls and sticks cartoon), feed second-principles models where only some degrees of freedom are considered (for instance, the soft mode in every unit cell, represented by the arrows or the springs in the cartoons). Parameters for the phenomenological Devonshire-Ginzburg-Landau methods can be determined from atomistic methods. The arrows in red stress the interconnection between experiments and theories at the different levels.

scopic mechanisms that are responsible for ferroelectric phase transitions, and to provide a firmer theoretical basis to existing classical theories.

Special attention was given to the interplay between the electronic and lattice-dynamical properties, with the intention of clarifying the physical nature of the structural instability. The classical groundbreaking work along these lines is due to Cochran [25], who first realized the importance of lattice dynamics in describing the ferroelectric distortion, and established the important concept of *soft mode* as the basic ingredient in the theory.

The explanation focuses on a special class of ABO_3 ferroelectric oxides: those where the B-site cation is formally in a d^0 oxidation state (common examples are $BaTiO_3$, $KNbO_3$). This means that “true” d electrons are, in principle, absent from the compound. Nevertheless, the occupied O ($2p$) and the empty B (d) orbitals partially hybridize, producing a bonding of mixed ionic-covalent

nature [26, 136]. A key observation here is that these hybridizations are very sensitive to the O-B distance. Based on this remark, Harrison [58] predicted a dynamical transfer of electronic charge when the atoms are displaced.

To understand qualitatively why this happens, it is useful to introduce the concept of *Born effective charge*, i.e. the polarization linearly induced by a small displacement of the atom α within zero macroscopic electric field [51]. For the sake of simplicity, if we consider a one-dimensional system it can be written as

$$Z_{\alpha}^{*} = \left. \frac{\partial P}{\partial x_{\alpha}} \right|_{E=0} \quad (5)$$

Within an extreme rigid-ion model, the Born charges coincide with the static charge of the model ion (the “nominal” value), while in a real material the Born charges account for electronic effects as well [154]. In the case of ABO₃ ferroelectrics, for example, the aforementioned O-B hybridization implies that the electronic valence orbitals do not follow rigidly the atom they belong to, but also significantly *polarize* in response to the displacement. As a consequence the Born charges are strongly “anomalous” [224, 151] as shown in Fig. 3(a) for BaTiO₃, i.e. a displacement of a given atomic sublattice gives rise to a spontaneous polarization that is much larger than that predicted by the static nominal charges. A first-principles based band-by-band decomposition clearly demonstrates the link between the O *2p*-B *d* hybridization and the giant dynamical charges [49, 48].

The anomalously large Born effective charges have profound consequences on the lattice dynamics. The relevant phonons here are the transverse modes at the zone center (Γ point), where all equivalent atoms in every unit cell are displaced by the same amount [see Fig. 3(b)]. Following the original idea of Cochran, the leading contributions to the phonon frequencies can be separated into short-range and long-range as follows. A giant dynamical charge implies a large long-range dipole-dipole interaction, which in turn tends to “soften” the optical phonons of the crystal where the O and B cations move in antiphase. In addition to this electrostatic term (which destabilizes the centrosymmetric configuration and thus favors ferroelectricity) we have the short-range repulsion between the ionic cores, which has the opposite effect. The stability or instability of the ferroelectric mode is ultimately decided by the delicate compensation of stabilizing short-range forces and destabilizing dipole-dipole interactions (see Fig. 1 of Ref. [50]). Whenever the latter prevail, the frequency ω of the lowest transverse optical mode becomes imaginary, so that $\omega^2 < 0$, which reflects the negative curvature at the origin of the total energy surface as a function of the mode amplitude (this is the origin of the term *soft mode*). As this delicate balance between short- and long-range forces is very sensitive to small modifications of the volume or of the Born effective charges [50], the strength (or the very presence) of the instability can vary greatly from one perovskite to another. This can be taken as a first-principles confirmation of the old hypothesis formulated by Slater [179] who suggested that the ferroelectric behaviour of BaTiO₃ might be caused by long-range dipolar forces that (via the Lorentz local effective field) would destabilize the high-symmetry configuration (the latter would be stabilized by more localized forces). The softening of a transverse optic mode has been experimentally confirmed by spectroscopic techniques [57, 164].

In the particular case of BaTiO₃ discussed above, which is the paradigmatic example of a ferroelectric perovskite oxide, both the short-range and dipolar

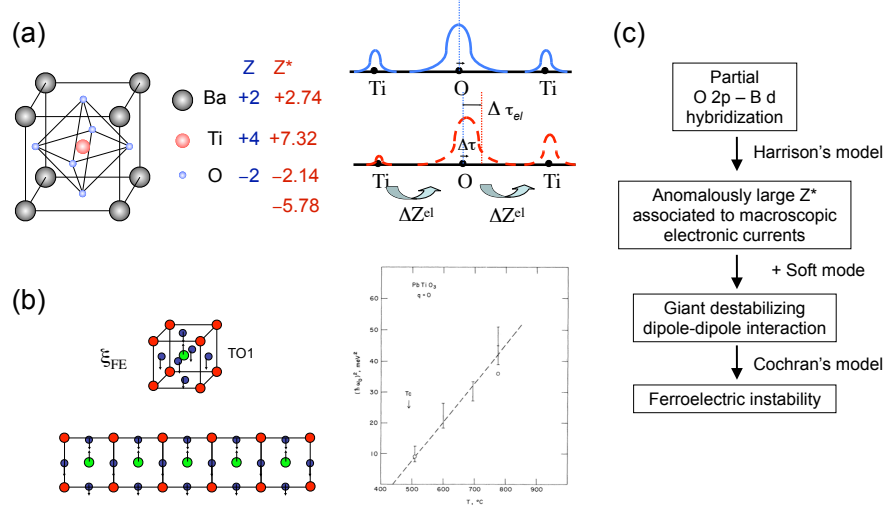


Figure 3: (a) The concept of Born effective charge Z^* illustrated for the case of BaTiO_3 . Z_α^* is equal to the polarization linearly induced by a small displacement of each atom α within zero macroscopic electric field [51]. In a purely ionic system, the Born charges coincide with the static charges Z , while in a real material the Born charges account for non-trivial electronic effects as well [154]. The Ti-O hybridization in BaTiO_3 implies that the electronic valence orbitals do not follow rigidly the atom they belong to, but also significantly *polarize* in response to the displacement. As a consequence the Born charges are strongly “anomalous” [224, 151], i.e. a displacement of a given atomic sublattice gives rise to a spontaneous polarization that is much larger than that predicted by the static nominal charges. (b) Illustration of the ionic displacements corresponding to the soft mode. The structural distortion ξ_{FE} is represented in a perovskite unit cell and corresponds to the displacement of the B and O atoms with respect to the A atoms. The local cooperative pattern of such atomic displacements corresponds to one of the transverse optic modes and is usually referred to as the *soft-mode*, as the frequency ω associated to this mode will become imaginary (so that $\omega^2 < 0$), as illustrated by the experiment on PbTiO_3 from ref. [178]. (c) Flowchart summarizing the connection between the O 2p–B d cation hybridizations and the ferroelectric instability of ABO_3 ferroelectric perovskite oxides.

parts of the interatomic interactions are highly anisotropic, and therefore the correlation of the atomic displacements is much stronger along the Ti-O chains. This concept of “chain instability” also applies to other materials like bulk KNbO_3 . Other compounds like e.g. PbTiO_3 present significant differences and deserve a separate discussion. For example, the A-site cation in both BaTiO_3 and KNbO_3 is usually considered to be chemically inert; conversely, Pb has a significant covalent interaction with oxygen. As a consequence, the correlations of the atomic displacements in PbTiO_3 appear to be much more isotropic. More importantly, the substantial role played by the A-site cation in the ferroelectric instability of Pb-based (and Bi-based) compounds in practice lifts the tradi-

tionally assumed requirement of d^0 -ness in the B-site cation. This observation opened new avenues of research in the context of multiferroics materials, where d electrons are essential or the compound will not be magnetic [62]. In recent years, many different mechanisms for ferroelectricity emerged, that depart even more drastically from the original soft-mode picture by Cochran; this is a very lively and active area of research, whose coverage goes unfortunately beyond the scopes and size limitations of the present work.

In summary, the driving force of conventional ferroelectric transitions can be understood in terms of the anomalously large Born effective charges, that couple to the atomic displacements via a giant dipolar interaction and produce an unstable “soft” phonon mode [see Fig. 3]. The large anomalous charges, in turn, emerge from the hybridization between O $2p$ and B-cation d orbitals, which is responsible for the polarization of the valence orbitals upon atomic displacement.

It is important to emphasize the *cooperative* nature of the ferroelectric phenomena: a single atomic displacement is not enough to trigger the ferroelectric distortion in a crystal. Only the cooperative displacement of a group of atoms inside the *correlation volume* is enough to induce the ferroelectric instability [46]. It is natural then to expect that this delicate balance will be modified in thin films, where the correlation volume is truncated. We shall address this point in the following section.

5 Theory of ferroelectric thin films

As discussed above, ferroelectricity can be in many cases linked to spontaneous atomic off-center displacements, resulting from a delicate balance between long-range dipole-dipole Coulomb interaction and short-range covalent repulsions. In ultrathin films and nanostructures, both interactions are modified with respect to the bulk. Short-range interactions are modified at surfaces and interfaces, due to the different chemical environment (chemical boundary conditions). Long range interactions are truncated due to lack of periodicity and is strongly dependent on the electrical boundary conditions. As stated above, the ferroelectric instability is also strongly sensitive to strain and will be influenced by mechanical boundary conditions such as epitaxial strains. These different factors can act independently to either enhance or suppress ferroelectricity.

For many years, samples below a certain size did not display ferroelectricity. It turned out that the reason for this suppression was not because of intrinsic size effects, but rather due to difficulties in fabrication. The fact that the experimentally obtained minimum thickness for a ferroelectric thin film has decreased by orders of magnitude over the years is a clear sign that for the most part the suppression was due to limitations in sample quality. For example, dead layers (incomplete screening), misfit dislocations and partial relaxation of the lattice, grain boundaries and defects such as oxygen vacancies are all known to strongly influence the ferroelectric properties.

In what follows we briefly summarize the most important concepts behind those different boundary conditions and their influence on the ferroelectric properties. For a more complete and detailed description of recent experimental and theoretical works on ferroelectricity in nanostructured materials and thin films, we refer the reader to recent book chapters [52, 146, 98] and topical review

papers [29, 144, 134, 38, 166, 173, 72, 229, 156].

5.1 Mechanical boundary conditions: strain

The coupling between ferroelectric polarization and strain is well known to be especially strong in ferroelectric perovskite oxides, and can have a substantial impact on the structure, transition temperatures, dielectric and piezoelectric responses. Exhaustive discussions on strain effects in ferroelectric thin films can be found in Ref. [163] (combined experimental and theoretical report), and in Refs. [144] and [37] (more focused on the theoretical point of view).

In ferroelectric thin films, homogeneous biaxial strain can be achieved thanks to the epitaxial growth of the film on a substrate with a different lattice parameter. Assuming perfect coherency, the strain is defined as a function of the bulk lattice parameters of the film material, a_f , and of the substrate, a_s , as $\eta = \frac{a_s - a_f}{a_f}$. The clamping between the film and the substrate onto which it is deposited can be maintained only in ultrathin films, where the elastic energy stored in the overlayer is still relatively small. For thicker films a progressive relaxation will occur via formation of misfit dislocations, which generally cause a degradation in film quality. Note that, in general, the strain state of the film will also depend on the thermal evolution of the lattice parameters from the deposition temperature to the measurement temperature, and the degree to which full lattice coherence has been developed and maintained during film growth.

In a simplified theoretical model [72], the main effect of the “polarization-strain” coupling is the renormalization of the quadratic term of the free energy, like the one shown in Eq. (3). So, playing properly with the epitaxial strain conditions, it is possible to make the coefficient α_2 more negative (further stabilizing the ferroelectric state or even inducing ferroelectricity in a non-ferroelectric material), or to make α_2 positive, thus suppressing the ferroelectric character of the film.

The first milestone theoretical work on the influence of strain on the ferroelectric polarization was by Pertsev *et al.* [130], who identified the correct “mixed” mechanical boundary conditions of the problem (fixed in-plane strains, and vanishing out-of-plane stresses), and computed the corresponding Legendre transformation of the standard elastic Gibbs function to produce the correct phenomenological free-energy functional to be minimized. Then they introduced the concept, now known as “Pertsev phase diagram”, of mapping the equilibrium structure as a function of temperature and misfit strain, which has proven of enormous value to experimentalists seeking to interpret the behaviour of epitaxial thin films and heterostructures.

These kind of diagrams were produced for the most standard perovskite oxides [BaTiO₃ [130, 131, 24], PbTiO₃ [130], SrTiO₃ [127, 128, 56], and Pb(Zr_x-Ti_{1-x})O₃ (PZT) solid solution [126]]. This approach generally yields very accurate results around the temperature/strain regime in which the model parameters were fitted (usually near the bulk ferroelectric transition). In distant strain-temperatures regimes the uncertainty tends to increase and, as reported for BaTiO₃, different sets of DGL parameters may provide qualitatively different phase diagrams [130, 131].

On the first-principles front, studies of misfit strain effects in single-domain perovskite-oxide thin films have been successfully carried out for several materials, most notably BaTiO₃ [35], PbTiO₃ and PbTiO₃/PbZrO₃ superlattices [15],

and SrTiO_3 (including the tunability of its dielectric response [3]). Full sequences of epitaxially-induced phase transitions and the values of the corresponding critical strains for eight different perovskites were reported in Ref. [34]. Strain-induced ferroelectricity in an otherwise non-ferroelectric material was also theoretically predicted in simple rocksalt binary oxides (BaO and EuO) and superlattices (BaO/SrO) [12].

From all these theoretical studies, a general trend emerged for perovskite oxides strained on a (001) substrate [34]: sufficiently large epitaxial compressive strains tend to favor a ferroelectric c -phase with an out-of-plane polarization along the [001] direction; conversely, tensile strains usually lead to an aa -phase, with an in-plane P oriented along the [110] direction. The behavior in the intermediate regime is material-dependent, but the general trend is that the polarization rotates continuously from aa to c passing through the [111]-oriented r -phase. In non-ferroelectric perovskites like SrTiO_3 and BaZrO_3 the intermediate regime is non-polar, while in PbTiO_3 the formation of mixed domains of c and aa phases could be favorable.

From the experimental side, there have been impressive advances as well. Thanks to the availability of several perovskite substrates with a wide variety of in-plane lattice parameters, we can now tune the ferroelectric and related properties in thin films by using the homogeneous strain almost as a continuous knob, which led to the coining of the term “strain-engineering”. For instance, Haeni *et al.* [56] observed room-temperature ferroelectricity in SrTiO_3 with an in-plane component of P . The effect can be rationalized in terms of the +1% tensile strain imposed by the DyScO_3 substrate, and is rather dramatic considering that SrTiO_3 is paraelectric in the bulk. Another example of strain-engineering was demonstrated by Choi *et al.* [24], with a large enhancement of ferroelectricity induced in strained BaTiO_3 thin films epitaxially grown on single-crystal substrates of GdScO_3 and DyScO_3 . The strain resulted in a ferroelectric transition temperature nearly 500 K higher than the bulk one and a remnant polarization at least 250% higher than bulk BaTiO_3 single crystals. Very recently, a spectacular strain effect was demonstrated both experimentally and theoretically [223, 59]: multiferroic BiFeO_3 films undergo an isosymmetric phase transition to a tetragonal-like structure with a giant axial ratio [6] when grown on a highly compressive substrate such as LaAlO_3 . Furthermore, both phases appear to coexist [223] in some conditions, with a boundary that can be shifted upon application of an electric field. This appears to be by far the largest experimentally realized epitaxial strain to date, of the order of 4-5 %; the existence of this new phase of BiFeO_3 was also predicted to be promising for enhancing the magnetoelectric response of this material [215].

Finally, in the last few years groundbreaking works have proposed new mechanisms, based on the coupling of spin, optical phonons and strain to design new multiferroic materials in which magnetic (electric) polarization can be induced by an applied electric (magnetic) field [39]. In some antiferromagnetic paraelectric insulators, there is a coupling between infrared-active phonons and magnetism. In this case, it might happen that the lowest frequency polar modes become unstable at a critical strain, producing an epitaxial-strain-induced ferroelectricity in the antiferromagnetic state. The strain is not only coupled with the polarization but also with the magnetic ordering. If the ferromagnetic spin alignment softens more a low-frequency polar mode that is strongly coupled to epitaxial strain, then the energy of the ferromagnetic-ferroelectric structure might

drop below those of the antiferromagnetic-ferroelectric phase for a given value of strain. This spin-phonon coupling mechanism for epitaxial-strain-induced multiferroelectricity has been theoretically proposed for SrMnO_3 [94] (critical tensile strain of +3.4 %), and EuTiO_3 [39], whose experimental demonstration was made only recently [93] (critical biaxial strains of -1.2 % under compression and +0.75 % under expansion).

As mentioned above, coherency between the substrate and the thin films lattice constants can be maintained only up to a limiting thickness, after which defects and misfit dislocations start to form. Strain relaxation leads to *inhomogeneous* strain fields (or strain gradients), which can have profound consequences on the properties of the thin film. A strain gradient intrinsically breaks the spatial inversion symmetry and hence acts as an effective field, generating electrical polarization even in centrosymmetric materials. This phenomenon became known as *flexoelectricity*, by analogy with a similar effect in liquid crystals, and is allowed in materials of any symmetry. Strain-gradient-induced polarization has, for instance, been measured in single crystals of SrTiO_3 , a non-polar material [228].

Flexoelectric effects can play an important role in the degradation of ferroelectric properties [20, 17] and therefore proper management of strain gradients is crucial to the performance of ferroelectric devices. At the same time, an increasing amount of research is now aimed at exploiting flexoelectricity for novel electronic devices. The possibility of generating a flexoelectric response in any dielectric material [79], irrespective of its symmetry, by carefully engineering strain gradients has generated a lot of excitement in the field (see, for instance, the review by L. E. Cross [27]). At the same time, fundamental questions about flexoelectricity are not completely settled, and modern first-principles-based approaches [153, 63] are being developed to revisit existing phenomenological theories from a microscopic perspective [195, 196].

5.2 Electrical boundary conditions: imperfect screening

The depolarization field arising from unscreened bound charges on the surface of a ferroelectric thin film is generally strong enough to suppress the polarization completely and hence must be reduced in one of a number of ways if the polar state is to be preserved (see Fig.4). Much of the research on ultrathin ferroelectrics thus deals directly or indirectly with the question of how to manage the depolarization fields. The screening can be obtained by free charges from metallic electrodes, ions from the atmosphere or mobile charges from within the semiconducting ferroelectric itself. Note that even in structurally perfect metallic electrodes, the screening charges will spread over a small but finite length, giving rise to a non-zero effective screening length λ_{eff} that will dramatically alter the properties of an ultrathin film. The problem of imperfect screening and how to model it will be addressed here. Later, we will see that even in the absence of sufficient free charges, the ferroelectric has several other ways of preserving its polar state, e.g., by forming domains of opposite polarization, or rotating the polarization into the plane of the thin ferroelectric slab.

It is well known that in most experiments on thin-film perovskite capacitors the electrical properties of the device tend to be plagued by deleterious size effects. In the paraelectric regime (i.e. above the Curie temperature) the measured capacitance tends to be orders of magnitude smaller than expected

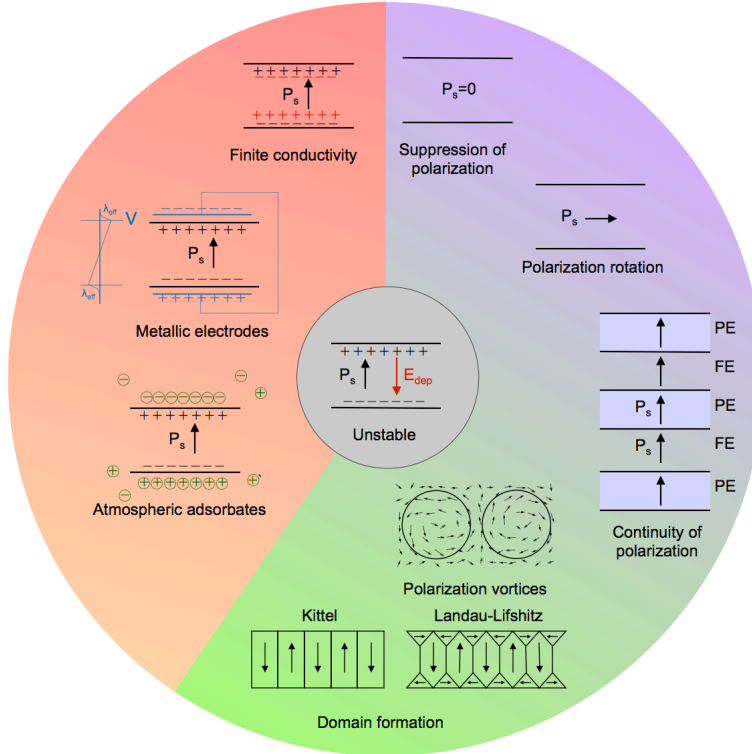


Figure 4: The depolarization field arising from unscreened bound charges on the surface of the ferroelectric is generally strong enough to suppress the polarization completely and hence must be reduced in one of a number of ways if the polar state is to be preserved. Much of the research on ultrathin ferroelectrics thus deals directly or indirectly with the question of how to manage the depolarization fields. The left part of the diagram illustrates screening by free charges from metallic electrodes, atmospheric adsorbates or mobile charges from within the semiconducting ferroelectric itself. Note that even in structurally perfect metallic electrodes, the screening charges will spread over a small but finite length, giving rise to a non-zero effective screening length λ_{eff} that will dramatically alter the properties of an ultrathin film. Even in the absence of sufficient free charges, however, the ferroelectric has several ways of preserving its polar state, as shown in the right part of the diagram. One possibility is to form domains of opposite polarization that lead to overall charge neutrality on the surfaces (Kittel domains) or closure domains (Landau-Lifshitz domains). Under suitable mechanical boundary conditions, another alternative is to rotate the polarization into the plane of the thin ferroelectric slab. In nanoscale ferroelectrics polarization rotation can lead to vortex-like states generating “toroidal” order. In heterostructures such as ferroelectric(FE)-paraelectric(PE) superlattices, the non-ferroelectric layers may polarize in order to preserve the uniform polarization state and hence eliminate the depolarization fields. If all else fails, the ferroelectric polarization will be suppressed.

from the classical formula $C = \epsilon S/t$, where ϵ is the dielectric constant of the insulator, t is the thickness of the dielectric layer, and S the surface area of the capacitor plates. In the ferroelectric regime the remnant polarization decreases with the thicknesses of the film [118, 99, 69, 75, 209]. Eventually, the film loses its ferroelectric properties below a certain *critical thickness* [71, 72], or alternatively breaks into domains of opposite polarization [117] (we shall present a more extensive discussion of domains in Sec. 6). The Curie temperature, T_c , itself tends to shift to lower values, and the dielectric anomaly (which in bulk is a sharp peak, directly correlated to the ferroelectric transition) is smeared out so that interpretation of the measurements is sometimes difficult [210, 106]. Fast relaxation of the polarization back to an unpolarized state after switching off the poling bias was reported [74]; the coercive field itself is known to be significantly larger compared to the bulk value.

Traditionally, the origin of these size effects was attributed to the existence of a physically and chemically distinct passive layer with degraded ferroelectric properties (and/or with smaller permittivity than the film material) at the ferroelectric/electrode interface, the so-called “*dead layer*”. Many processing issues can lead to the formation of such a passive layer. For example, damage can be created at the film surface by bombardment of the sputtering ions during the deposition of a top electrode [89], or by changes in stoichiometry due to the loss of volatile elements such as lead or oxygen. A non-switching dead layer [89, 114, 198] can also derive from pinning of domain-walls [90], or the screening of the internal field by a depletion region [197]. The formation of oxygen vacancies during growth can be another important factor to be cautious about, as they might lead to the presence of space charge in the film; the detrimental consequences of space charge near the surface have been known since the work of Känzig in 1955 [73]. Note that in general oxygen vacancies seem to be implicated in most of the failure mechanisms of ferroelectric capacitors, e.g. their redistribution with electrical cycling is believed to be the main cause of polarization fatigue [221, 30, 105].

While the above arguments have traditionally supported an extrinsic origin of the dead layer, more recently increasing attention has been paid to possible intrinsic effects. Indeed, the improvement of growth techniques and the widespread use of metallic perovskites as electrode materials have allowed for the realization of capacitor structures with nearly ideal lattice-matched interfaces. In these high-quality films the aforementioned processing concerns were minimized, but the size effects turned out to still be significant. This suggests that even an ideal ferroelectric/metal interface might be characterized by an effective “dead layer”; this would stem from the fundamental quantum-mechanical properties of the junction rather than from growth-induced defects. Before the advent of first-principles simulations for this class of systems, a popular semiclassical model invoked the finite Thomas-Fermi screening length, λ_{TF} , of realistic electrodes (as opposed to an ideal metal, which would perfectly cancel the surface polarization charges of the ferroelectric) [10]. This would create a spatial separation between bound charges and screening free charges, i.e. it would act as a capacitance in series with the film, with detrimental effects that are in all respects analogous to those of a physically degraded layer near the interface. In fact, the idea of an imperfect screening has considerable history; in the 70s [112, 4, 5, 219], within the framework of the Landau theory, researchers at IBM found that a finite λ_{TF} would lead to the appearance of a residual depo-

larization field, change the order of the phase transition, reduce the magnitude of the polarization and shift the transition temperature.

At the *microscopic* level the reliability of these semiclassical arguments is, however, unclear. Contrary to the case of a doped semiconductor, λ_{TF} in typical electrode materials is fairly small, usually 0.5 Å or less. This implies that the Thomas-Fermi screening would occur in a region that lies adjacent to the interface plane, where the properties of the electrode material are far from bulk-like. The use of bulk electrode parameters in such a context (e.g. λ_{TF}) appears therefore unjustified. Furthermore, the quantum-mechanical penetration of conduction states into the insulating film might (at least partially) cancel the effects of a finite λ_{TF} ; this is usually neglected in semiclassical models. Finally, interface-specific effects and chemical bonding may be as important as purely electronic effects; again, these effects are absent from the simplified Thomas-Fermi treatments.

First-principles theory have played a leading role in recent years at addressing the above questions with unprecedented accuracy, as in a typical density-functional calculation all the electrostatic and chemical effects occurring at a realistic interface are automatically included at a fundamental, unbiased level. The seminal works of Ref. [71] and Ref. [186] have demonstrated, with fully quantum-mechanical calculations, the existence of an interface-related depolarization effect in ferroelectric and paraelectric capacitors, respectively. Many works have followed during the past few years, pointing out important aspects of the problem, such as the ionic contribution to the screening (predicted in Refs. [158, 47] and experimentally observed by high-resolution transmission electron microscopy in Refs. [66, 22]), or the role of the electrode material in aggravating or reducing the size effects [158, 186]. The findings of these investigations can be roughly summarized into three main messages: (i) an “intrinsic dead layer” is, in general, present even at perfect, defect-free interfaces [186]; (ii) the magnitude of the depolarization effect is an *interface* property (i.e. it depends on materials, crystallographic orientation and lattice termination), and is best described as an *effective screening length* λ_{eff} (or, equivalently, interface capacitance) that includes all the electronic and ionic effects described above; (iii) that use of simple-metal electrodes (such as Pt or Au) is almost systematically predicted to be beneficial for the electrical properties of the device as compared to oxide electrodes. Point (iii) above is particularly puzzling in light of the experimental results, which show a much better performance when oxide electrodes (e.g. SrRuO_3) are used. The use of SrRuO_3 was indeed an experimental breakthrough in that it allowed for a drastic reduction of fatigue issues [148, 147]. It is important to stress that the first-principles results are relevant for an ideal, defect-free interface; this is, unfortunately, very challenging to realize in practice in the case of Pt electrodes. In addition to the practical question “Which electrode is better?”, first-principles theory is able to answer more fundamental (and maybe more interesting) ones, such as: “Why are ideal simple-metal electrode/ferroelectric interfaces behaving better?” We shall come back to this point in Sec. 5.4; in the following Section we first briefly discuss the consequences of a finite λ_{eff} on the electrical properties of the device.

Before closing this Section on the microscopics of the polarization screening mechanism, it is useful to mention an increasingly large body of literature that concerns ferroelectric films with an open surface, i.e. without a top electrode. In this case, as there are no metallic free carriers available, adsorbates

or point defects [214, 182, 40, 82, 96] are believed to supply the compensating surface charges that are necessary to stabilize a polar state. Bringing these ideas one notch further, Wang *et al.* have recently demonstrated reversible and reproducible ferroelectric switching in a thin PbTiO_3 film by varying the partial oxygen pressure $p\text{O}_2$ at the open surface [212]. This breakthrough proof of concept was coined “chemical switching”.

5.3 Electrical functionals with a depolarization field

Whatever the microscopic origin of the depolarization effects, a typical parallel plate capacitor with non-ideal electrodes can be modeled in terms of a bulk-like film that is N unit cells thick, in series with two interfacial layers, of thickness λ_{I} , that behave like a linear dielectric material of dielectric constant ϵ_{I} . In the following, we assume an uniaxial ferroelectric and keep only one component of all the vector quantities. Then, the energy as a function of the electric displacement D can be written as the energy of the three capacitors in series: the two (assumed identical) interfaces and the bulk of the film (D can be viewed as the surface density of free charges stored on the plates) [185]:

$$U_N(D) = NU_{\text{b}}(D) + 2S\lambda_{\text{eff}}\frac{D^2}{2\epsilon_0}. \quad (6)$$

Here U_{b} is the bulk internal energy per unit cell at a given D , S is the cell cross-section, ϵ_0 is the free vacuum permittivity, and $\lambda_{\text{eff}} = \lambda_{\text{I}}/\epsilon_{\text{I}}$ is the effective screening length mentioned in the previous Section (only the ratio between λ_{I} and ϵ_{I} is physically relevant). The equilibrium monodomain state of such a capacitor in short-circuit is readily obtained by imposing $dU_N(D)/dD=0$, which leads to the condition $NdU_{\text{b}}/dD = -2S\lambda_{\text{eff}}D/\epsilon_0$. Note that the internal (“depolarization”) field in the bulk-like region is *defined* as $\Omega\mathbf{E}_{\text{d}} = dU_{\text{b}}/dD$, where $\Omega = Sc$ is the unit cell volume and c is the out-of-plane lattice parameter. Note also that in typical ferroelectrics the electric displacement can be very accurately approximated with P_0 , the ferroelectric polarization associated to the soft mode; then, by writing the total thickness $t = Nc$ we obtain the depolarization field,

$$\mathbf{E}_{\text{d}} = -\frac{2\lambda_{\text{eff}}P_0}{\epsilon_0 t}, \quad (7)$$

From Eq. (7) we see that the depolarization field depends linearly on the effective screening length and the polarization, P_0 , and is inversely proportional to the film thickness t . The minus sign means that the field opposes to the polarization. The field has to remain small enough in order to stabilize a monodomain polar state in the capacitor. All the quantum effects and the chemistry at the interface are embedded in the only parameter λ_{eff} , that will depend on the ferroelectric material, the electrode, the atomic structure and the particular orientation of the interface. An alternative derivation of Eq. (7) can be found in Ref. [28, 52, 72], and a detailed comparison between the expressions given by different models is available in Ref. [52].

As it is clear from previous discussions, the electrical boundary conditions are extremely important in the stabilization of the different phases and on the functional properties of the capacitors. It also appears clear that layered geometries such as capacitors or monodomain superlattices can be very effectively described

within a simple series capacitor model, where D is the fundamental electrical variable, while using E would impose short-circuit boundary conditions across the whole simulation box due to the overall periodicity of the system. In this context, the recently-developed first-principles techniques (discussed earlier in the Chapter) to treat D as the fundamental electrical variable [187, 189] appear ideally suited to perform this kind of decomposition.

The preservation of D across the heterostructure leads a “locality principle”, where the local bonding effects can be unambiguously separated from the long-range electrostatics interactions, allowing for a detailed analysis of the microscopic mechanisms contributing to the polarization. This opens the door to LEGO-like models, where the electrical properties of *individual* atomic layers [217], even including oxygen octahedra rotations [216], are computed and stored as a function of the in-plane strain and electric displacement, and combined afterwards in arbitrary manners to predict polarization or nonlinear dielectric response of user-designed superlattices.

5.4 Chemical-bonding contributions to the electrical boundary conditions

We have seen in the previous sections that, in standard ferroelectric capacitors, the electrode/ferroelectric junction generally introduces an additional term in the electrostatic energy functional of the film. First-principles simulations demonstrated that such a term, which typically tends to suppress ferroelectricity via a depolarization field in zero bias, is present even in the case of a perfect defect-free interface, where it was shown to depend on the microscopic details of the junction. What we have not discussed yet is the precise relationship between these microscopic properties (e.g. local electronic and ionic structure, chemical bonding, etc.) and the macroscopically relevant quantities, e.g. λ_{eff} . Such an analysis was performed in two recent first-principles works, [188, 189] where the techniques to work at constant D were used to achieve a local decomposition between bulk and interface contributions to the electrical equation of state of a thin-film capacitor. Based on this decomposition, the interface-specific ingredients could be singled out, as we shall explain in the following.

First, recall that the traditional phenomenological understanding of the imperfect screening at a metal/ferroelectric interface was based on a Thomas-Fermi model of the free carriers in a real metal, i.e. on purely *electronic* effects. It is not difficult to realize that this gives only a partial picture, and that chemical bonding effects should be taken into account as well – possibly even more seriously than electronic ones. Why? Because the high dielectric constant ϵ of perovskite ferroelectrics is largely dominated by lattice polarization. The ionic lattice mediates a contribution of the type $\Delta\epsilon \sim (\bar{Z}^*)^2/\omega^2$, where ω and \bar{Z}^* are the frequency and the Born effective charge of a given zone-center optical mode. As the soft-mode frequency goes to zero, $\Delta\epsilon$ tends to diverge. Now recall that the vanishing frequency of the soft mode results from a subtle balance between long-range and short-range forces. If at the interface we create strong chemical bonds between the film and the electrode, we inevitably stiffen the short-range part, and this might raise ω considerably. This would create an interface oxide layer with lower local ϵ , i.e. a dielectric “dead layer”. Conversely, if one carefully engineers the interface in such a way that the metal/oxide bonds are loose, then the interface-related suppression of the local dielectric constant should be

minimized, or even completely avoided. In principle, this picture suggests an even more tantalizing possibility, that is, of making the interface bonds loose enough that the surface unit cell becomes ferroelectrically active, possibly even more so than the bulk film material itself. This would constitute a drastic departure from the conclusions of the Thomas-Fermi theory, which systematically predicts a deleterious depolarization effect at a metal/ferroelectric interface.

As unrealistic as it may sound, such a scenario was recently demonstrated by means of first-principles calculations in Refs. [188, 189]. These works focus on BaO-terminated BaTiO₃ thin films that are symmetrically sandwiched between two Pt electrodes. At this interface the Ba and O atoms that terminate the BaTiO₃ lattice sit atop the square lattice of Pt atoms at the (100)-oriented electrode surface. Pt chemically binds to O, while it repels Ba. This competition stretches and weakens the Pt-O bond, that becomes “ferroelectrically active”. This mechanism produces an enhancement of the overall ferroelectricity of the capacitor, which becomes stronger the thinner the film. At the extreme limit of a two-unit cell BaTiO₃ film the spontaneous (and *switchable*) polarization is 35 % larger than the bulk BaTiO₃ value. [188] This implies an opposite behavior to the traditional “dead layer” effect, which could be rationalized within the electrostatic model of the previous section by assuming a *negative* λ_{eff} . The AO-terminated perovskite/simple metal interface is of course a very specific interface structure, that might or might not be representative of the experimentally realizable stable configurations. It was mainly chosen as a proof of principle, i.e. as a testcase where the ideas sketched in the above paragraphs happen to manifest themselves in a particularly dramatic way. It should be kept in mind that the above principles about the relationship between bonding and dielectric properties are completely general, and we expect them to play an important role at *any* metal/ferroelectric interface. We stress that the macroscopic electrical parameter λ_{eff} does include implicitly all the effects of chemical bonding, together with purely electronic contributions. In that sense, it is not entirely appropriate to speak of “chemical boundary conditions” as something distinct from the electrical boundary conditions: the former are best understood as chemical-bonding contributions to the latter.

6 Polarization domains and domain walls

The previous section was concerned predominantly with ultrathin ferroelectrics sandwiched between metallic electrodes that provide the screening charges necessary to stabilize the ferroelectric ground state. Even in the absence of free charges, however, ultrathin ferroelectrics find a number of ways of preserving their polar state, as illustrated in Fig. 4. One possibility is to form domains of opposite polarization known as Kittel domains, or flux closure (Landau-Lifshitz) domains.

6.1 Kittel law

Domain formation in ferroelectrics is analogous to that of ferromagnets and thus most of the theory was adapted from the seminal works of Landau and Lifshitz [88] and Kittel [77, 78]. Domains lead to overall charge neutrality at the surfaces, eliminating the depolarization field, at least throughout the majority

of the ferroelectric slab, and reducing the electrostatic energy of the system. For Kittel domains (Fig. 4), the stray fields arising from the antiparallel arrangement of dipoles, are confined to a thin near surface region and decay exponentially over a lengthscale comparable to the domain width w . The electrostatic energy of these fields thus increases with domain size as

$$F_P \sim P_s^2 w, \quad (8)$$

favoring domains that are as small as possible. For Landau-Lifshitz domains (Fig. 4), a similar term linear in w exists but has its origin in the anisotropy energy—the cost of rotating the dipoles near the surface.

Decreasing the domain size, however, also increases the density of domain walls—the boundaries that separate domains of different polarization. Short-range dipolar interactions resulting from the modification of the dipole moments when passing through a domain wall give rise to an energy cost known as domain wall energy σ_W per unit area of the wall, and contribute a term that scales with domain wall density, i.e. as $1/w$ to the total energy

$$F_W = \sigma_W \frac{t}{w}, \quad (9)$$

where t is the thickness of the ferroelectric. Minimizing $F_W + F_P$ with respect to w gives the famous Kittel relation

$$w \sim \sqrt{t}. \quad (10)$$

As device dimensions shrink, so do the domains. Remarkably, the validity of this simple scaling law for ferroelectric materials extends over six orders of magnitude in t , as shown in Fig. 5 [19]. The constant of proportionality in (10) depends on a number of material properties, generally yielding much larger domain widths for ferromagnets than for ferroelectrics [161]. If the domain wall thickness T is taken into account, however, a universal dimensionless quantity w^2/Tt can be defined for all ferroic domains [166], see Fig 5.

Theoretically, the Kittel law has been demonstrated within the model Hamiltonian approach for $\text{Pb}(\text{Zr}_{0.4}\text{Ti}_{0.6})\text{O}_3$ thin films [86]. Perfect scaling according to this law was obtained for thicknesses above 4 unit cells. In PbTiO_3 , Streiffer *et al.* [192, 41] observed by in-situ x-ray synchrotron diffraction the evidence of 180° stripe domains with periods of 1.2-10 nm (going as $\sim \sqrt{t}$) in c -axis oriented thin films from 420 down to 12 Å thickness grown epitaxially and coherently on SrTiO_3 insulating substrates.

It is worth noting that Kittel's law can also be generalized to more complex three-dimensional shapes [18].

6.2 Domains morphology

For a long time it was believed that domains in ferroelectrics are of the Kittel type, due to the strong crystalline anisotropy that makes polarization rotation difficult. Recent theoretical work, however, has shown that significant polarization rotation is expected in many cases, particularly as dimensions are reduced, fuelling an intense experimental search for evidence of this. Building on earlier phenomenological theories [83, 9, 13, 132, 129, 14, 191], model Hamiltonian and

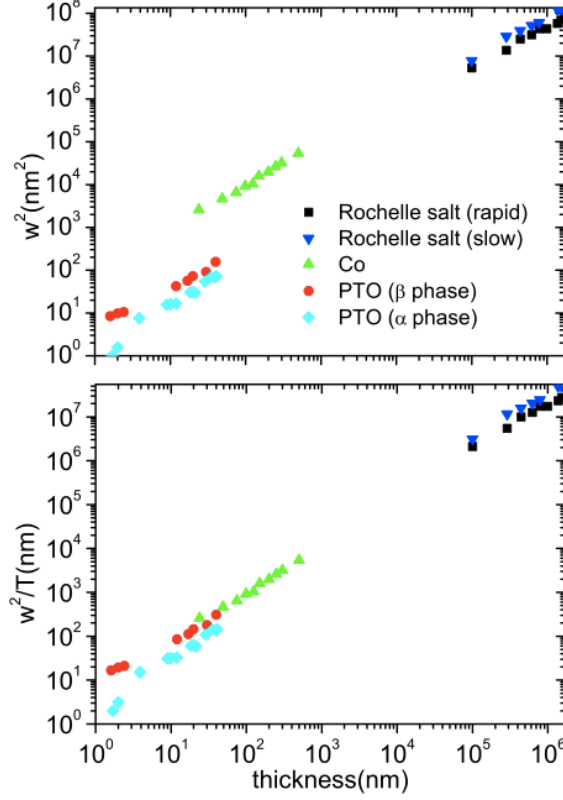


Figure 5: (Above) Square of the 180° domain width as a function of crystal thickness for some ferroics (data extracted from Ref. [115, 192, 60]). (Below) When the square of the domain size is divided by the wall thickness, all data fall on the same parent curve. The wall thicknesses used for the scaling have been extracted from Ref. [115, 64, 113]. Reprinted with permission from Ref. [19].

ab-initio calculations have revealed that the precise domain morphology is expected to depend strongly on the electrical and mechanical boundary conditions, and will in general be of a character that is intermediate between that of the Kittel and Landau-Lifshitz models [137, 86, 1, 174]. Static and dynamic properties of such stripe domains have been calculated for BaTiO_3 [202], PbTiO_3 , $\text{Pb}(\text{Zr,Ti})\text{O}_3$ [84, 87, 133, 218] and BiFeO_3 [141], as well as superlattices consisting of periodically alternating layers of BaTiO_3 and SrTiO_3 [103], giving important insight into the dependence of domain morphology on the precise crystalline and chemical structure of the material and revealing other types of domain patterns, such as “bubble nanodomains” [84]. The real picture is in addition complicated by the presence of disorder that affects both the static morphology and dynamic behavior of nanodomains [125, 16]. Experimental findings and theoretical understanding of ferroelectric (and ferroelastic) domains in bulk crystals and thin films developed during the past 60 years can be found in Ref. [199].

Reducing the dimension not just in one direction as is the case for ultrathin

films, but in two (nano-rods [206], -wires [222], -tubes [107]) or even the three directions in space (nano-dots [123, 162] and -particles [104]) leads to more complex domain patterns. Theoretical studies of ferroelectric nanoscale disks and rods [42, 120, 135, 142, 138, 139, 140] have revealed yet another mechanism for dealing with the depolarization field: formation of polarization vortices with zero net polarization, but a finite spontaneous toroid moment. This “ferroelectric” state does not seem to be affected by the surface local environments, unlike that of an ultrathin ferroelectric film. Interestingly, the toroid moment can be equivalently parallel or anti-parallel to the z -axis, and it is possible to switch from one minimum of the toroidal phase to the other by applying a time-dependent magnetic field (the magnetic field interacts with the total toroid moment of the nanoparticles by generating a curling electric field $\nabla \times E = -\partial B/\partial t$), inciting some researchers to dream about novel bistable devices based on toroidal order Ref. [143]. It is to be noted however that, although direct observations of vortex states in soft ferromagnetic nanodots and nanorings [177, 211, 23, 227] have been made, experimental evidence in ferroelectrics is much more scarce. A few recent experiments tend to confirm the existence of such toroidal polarization ordering, as for example in $\text{Pb}(\text{Zr,Ti})\text{O}_3$ nanodots observed by piezoresponse force microscopy [155]. Recent developments in spherical aberration correction for transmission electron microscopes have been invaluable in revealing polarization rotation for the first time with atomic resolution [122, 67]. Mesoscopic dipole closure patterns were revealed by piezoresponse force microscopy images on free-standing, single-crystal lamellae of BaTiO_3 [111].

6.3 Domain walls

Domain walls — the boundaries between domains — are interesting in their own. New experimental and theoretical work has revealed that they often possess fascinating structural and electronic properties that are absent in the parent material, opening an exciting possibility for novel devices based on the concept of domain wall engineering [160]. An interesting example is the observation of a sizeable spontaneous polarization in (100) twin walls in CaTiO_3 , a ferroelastic paraelectric material [54]. Possible polar ferroelastic domain walls have also been found in paraelectric SrTiO_3 [228]. Other remarkable phenomena have been observed, e.g., twin walls that can support superconducting currents within WO_{3-x} , an otherwise insulating material [2]. Our discussion here will focus on the domain walls in ferroelectric materials, and on the recent discovery that domain walls in multiferroic BiFeO_3 are conducting and can be used to obtain above-band-gap photovoltaic responses [167, 220].

BiFeO_3 is a largely studied multiferroic material, since at room temperature it is ferroelectric as well as anti-ferromagnetic. The polarization in BiFeO_3 is directed toward one of the 8 equivalent $\langle 111 \rangle$ directions in the pseudocubic unit cell. Combining these different polarizations into pairs of neighbors, it can be easily checked that there will be 3 different angles possible between two different polarizations: 180° , 109° and 71° . These define the three different types of domain walls that can be observed in BiFeO_3 at room temperature.

Using room temperature conductive atomic force microscopy, Seidel *et al.* [167] found surprisingly that 180° and 109° domain walls in BiFeO_3 are conducting, while 71° are not. To understand this observation, one might be naively tempted to invoke a “polar discontinuity” scenario, where a (hypothetical) orientation-

dependent discontinuity in P would induce a two-dimensional gas of conducting carriers. This is, however, not the case here: as a matter of fact, all these domain walls are charge-neutral, i.e. the normal component of the macroscopic P is preserved across the wall. Interestingly, high-resolution transmission electron microscopy images of a 109° domain wall reveal a small *local* increase in the Fe displacements (relative to the Bi lattice) perpendicular to the domain wall, within the same region where the parallel displacements invert their sign. An analogous displacement pattern was found in model DFT calculations of the same system, which further predict a step in the electrostatic potential of up to 0.18 eV. A potential step at BiFeO₃ walls was later found to be involved in carrier photogeneration processes [220], and it is therefore not unreasonable to think that it might also be responsible for the enhanced conductivity reported by Seidel et al.

To understand the origin of such an electrostatic potential step, it is useful to consider the simpler case of PbTiO₃, where the spontaneous polarization is oriented along (100). In the case of 180° domain wall in PbTiO₃, with a net polarization on either side, the metal cations act as a center of inversion symmetry; therefore, a dipole moment or a potential step are both forbidden. Conversely, in the case of 90° walls in PbTiO₃, the two sides of the domain wall cannot be related by any symmetry operation; a net dipole moment is allowed, and calculations indeed confirm the presence of an associated potential step [113]. Similar ideas would apply to BiFeO₃, although the situation here is slightly more complicated because of the (111) orientation of the spontaneous polarization.

As an alternative explanation for the enhanced conductivity, Seidel et al. also observed that at the wall the fundamental band gap of BiFeO₃ might be reduced with respect to that of a uniform domain. This hypothesis is again supported by the DFT data. A decrease in the band gap would modify the band offset with a conductive atomic force microscopy tip and possibly favor carrier injection. Whether the former or the latter mechanism dominates, or whether there are some further extrinsic mechanisms at play (e.g. defects) that were not considered by Seidel et al. remains an open question that is left for future studies.

7 Artificially layered ferroelectrics

An alternative approach to investigate and exploit the properties of ultrathin ferroelectrics has been to fabricate superlattices where ferroelectric and paraelectric layers as thin as a few unit cells alternate periodically to produce an artificially layered single crystal [194]. These seemingly simple nominally two-component heterostructures have been found to display a rich spectrum of functionalities arising from the interplay between the effects of strain, electrostatic interactions between the ferroelectric layers, and coupling of different structural instabilities in the reduced symmetry environment of the interfaces.

7.1 Electrostatic coupling

When thin ferroelectric layers are separated by paraelectric slabs, any discontinuity in the polarization will give rise to strong electric fields that tend to both

suppress the polarization in the ferroelectric layers and polarize the paraelectric component. The electrostatic energy cost associated with these fields is very large and thus the system will look for a more favorable ground state.

One possibility is to adopt a state of uniform out-of-plane polarization throughout the structure, as in Fig. 4. In a first approximation, we can think in terms of a continuum model, based on the bulk electrical and electromechanical properties of the constituents. Within this assumption, the value of the polarization will only depend on the relative fraction of the ferroelectric material and on the mechanical boundary conditions [121, 31]. For example, $[\text{BaTiO}_3]_1/[\text{SrTiO}_3]_4$ superlattices with just a single unit cell of BaTiO_3 per period were predicted to be ferroelectric, whereas in $[\text{BaTiO}_3]_2/[\text{SrTiO}_3]_3$ superlattices with 2 u.c. of BaTiO_3 and 3 u.c. of SrTiO_3 repeated periodically the polarization was even expected to exceed that of bulk BaTiO_3 due to the compressive strain imposed by the SrTiO_3 substrate [121]. Experimentally, the enhancement of ferroelectricity in such fine-period two-component superlattices has been reported by a number of laboratories around the world, e.g. Refs [175, 201, 200]. Similar behavior has also been observed in three-component $\text{BaTiO}_3/\text{SrTiO}_3/\text{CaTiO}_3$ superlattices [92]. *Ab-initio* studies suggest that the intrinsic inversion symmetry breaking in such “tricolor” heterostructures should lead to a built-in bias and self poling [159], with some experimental work supporting this prediction [213]. As the individual layers get thicker, however, domain formation becomes a more effective mechanism for eliminating the depolarization fields and lowering the total energy of the superlattice [102]. In $[\text{KNbO}_3]_n/[\text{KTaO}_3]_n$ superlattices, a crossover occurs when n exceeds about 7 u.c. from a regime where the KNbO_3 layers are electrostatically coupled by the continuity of the displacement field, as described above, to a state where the polarization is confined mainly to the ferroelectric layers with domains of opposite polarization screening the depolarization field [183, 190, 169]. Figure 6(a) shows the ferroelectric-to-paraelectric transition temperatures as a function of n . The strong electrostatic interlayer coupling in short-period (small n) superlattices means they behave as a single ferroelectric material with T_c independent of n . In larger period superlattices the ferroelectric layers decouple and the transition temperature scales with the layer thickness as in single ferroelectric films. The densely packed nanodomains, characteristic of these ultrathin ferroelectric layers, give rise to a large enhancement in the effective dielectric response as even tiny domain wall displacements under applied field can lead to large changes in polarization [230].

Relaxing the substrate-imposed epitaxial strain leads to more complex behavior (Fig. 7). In $\text{BaTiO}_3/\text{SrTiO}_3$ superlattices the BaTiO_3 layers will then impose a tensile strain on the SrTiO_3 , forcing it into a strain-induced ferroelectric phase with in-plane polarization [68, 70, 97]. The corresponding compressive strain experienced by the BaTiO_3 layers, on the other hand, reinforces the state with out-of-plane polarization. The interplay between mutual interlayer strains and the electrostatics demanding the continuity of the out-of-plane displacement leads to complex polarization rotation patterns and unusual domain structures, as shown in Fig. 7 [70, 91]. The morphologies and switching characteristics of domains in superlattices have already received significant attention from the theoretical community, but remain challenging to study experimentally.

While simple arguments based on continuum electrostatics and elasticity theory are remarkably successful in describing many of the features of these nanoscale heterostructures, other properties require a more sophisticated theo-

ries. Recent studies highlight the importance of non-polar structural distortions, such as oxygen octahedral rotations as well as the properties of the interfaces between the individual layers [217]. In short-period superlattices, genuine interfacial effects going beyond continuum electrostatic models become important. Quantifying these effects within first-principles theory became possible only recently, and the constrained D approach has been invaluable in decomposing the effects of electrostatics from those of short-range interactions [187]. For example, in tricolor $\text{BaTiO}_3/\text{SrTiO}_3/\text{CaTiO}_3$ superlattices, Wu et al. [217] found that interfaces tend to suppress ferroelectricity; that is, for a given relative fraction of the three constituents and a given value of the strain, P will tend to decrease for a higher density of interfaces. Interestingly, when octahedral rotations are allowed in the CaTiO_3 component of $\text{BaTiO}_3/\text{CaTiO}_3$ superlattices, interfaces appear to have a beneficial, rather than detrimental, effect [216].

More generally, a major breakthrough in this field came from the realization that the broken-symmetry environment of the interface can have dramatic consequences on the electrical properties of the system, for example by “activating” lattice modes that are non-polar in the bulk phases of either constituent. We shall illustrate this important concept in the following section, by focusing on the case of oxygen octahedral rotations in $\text{PbTiO}_3/\text{SrTiO}_3$ superlattices.

7.2 Engineering ferroelectricity at interfaces

It has long been noted that the interface between two materials often has properties of its own, and in short-period superlattices, where the interface density becomes high enough, the interfaces can dominate the behavior of the material [229]. Space charge accumulation and structural defects generally have detrimental effects [124, 55], and management of these extrinsic contributions is essential to uncover the more interesting intrinsic phenomena that arise at the interfaces.

The ideal cubic perovskite structure is stable only within a narrow range of ionic radii, and hence most ABO_3 perovskites are prone to a number of symmetry lowering instabilities. These include polar distortions, oxygen octahedron rotations and Jahn-Teller distortions. In PbTiO_3 , for instance, the polar and antiferrodistortive (AFD) instabilities compete and the condensation of the former suppresses the latter in bulk, whereas bulk SrTiO_3 is paraelectric but undergoes an AFD transition at around 105 K. While the different types of instabilities usually compete at the bulk level, ferroelectric (FE) and AFD modes can coexist at surfaces and interfaces, due to the asymmetric environment of the near surface atoms [116, 8]. In $\text{PbTiO}_3/\text{SrTiO}_3$ 1/1 superlattices epitaxially strained on SrTiO_3 substrates, it has been shown that the ground-state structure arises from the combined condensation of a FE distortion with amplitude P_z and two distinct non-polar AFD motions involving rotations of oxygen octahedra either in-phase or out-of-phase by angles ϕ_{zi} and ϕ_{zo} . These distortions are denoted respectively FE_z , AFD_{zi} and AFD_{zo} in Figure 8. Moreover, the symmetry relationship between these three distortions is such that it allows the appearance of an unusual trilinear coupling term, $-g\phi_{zi}\phi_{zo}P_z$, in the free energy expansion (Eq.3), similar to what happens in improper ferroelectrics [11, 95]. In cases where the non-polar modes are primary order-parameters, the effect of this linear term on the free energy is to induce a spontaneous polarization by shifting the energy versus polarization well to lower energy as illustrated schematically

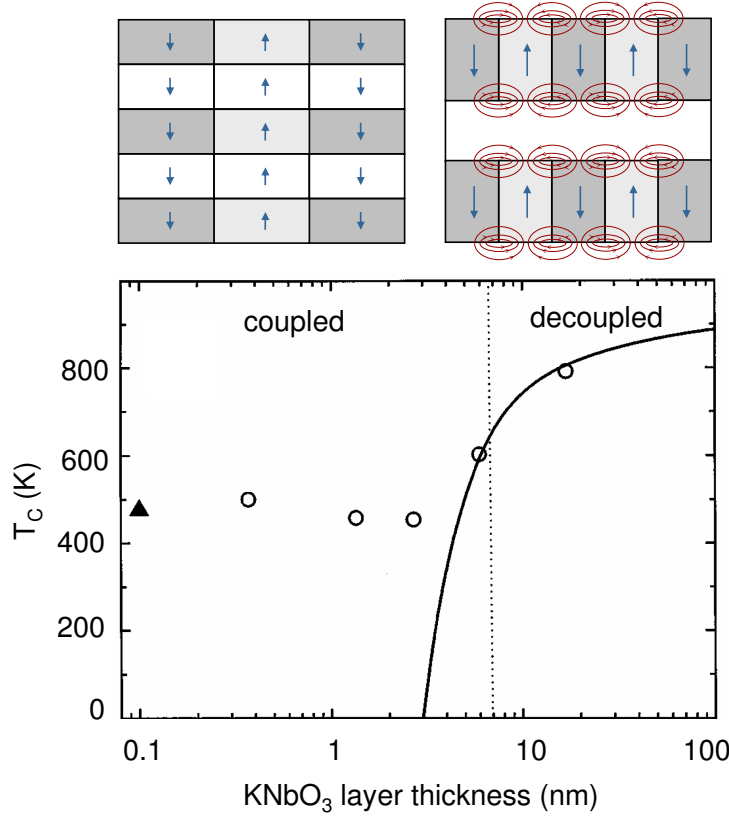


Figure 6: Evolution of the ferroelectric-to-paraelectric transition temperatures with n in $[\text{KNbO}_3]_n/[\text{KTaO}_3]_n$ superlattices, illustrating a transition from strong interlayer coupling with continuous polarization throughout the superlattice, to a decoupled state with polarization confined to ferroelectric layers [183, 190]. Top panels, after Fig. 1 of Ref. [190]. Bottom panel adapted with permission from Ref. [183].

in Figure 8. Improper ferroelectrics display a number of interesting and useful features such as temperature-independent dielectric permittivities [95] and reduced sensitivity to depolarization-field-driven size effects [157].

Such trilinear coupling of structural instabilities at interfaces is not restricted to artificial $\text{PbTiO}_3/\text{SrTiO}_3$ superlattices and several recent theoretical studies have focused on the search for alternative materials presenting similar behavior. It has been demonstrated through group theoretical arguments, for example, that in bicolor ABO_3 superlattices a similar trilinear coupling between structural instabilities can only be achieved by modulating the A-site cation lattice (not the B-site). Moreover, such a coupling is not restricted to artificial superlattices but can also appear in naturally-occurring layered perovskites like Ruddlesden-Popper or Aurivillius compounds [7]. The trilinear term produces an unusual coupling between FE and AFD modes in the sense that switching

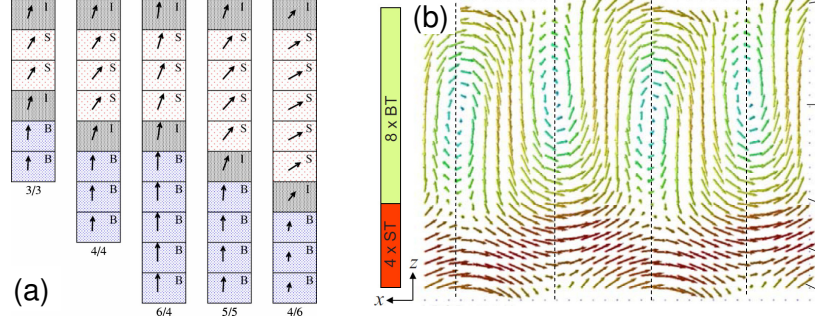


Figure 7: Theoretically calculated polarization distributions in BaTiO₃/SrTiO₃ superlattices: (a) monodomain with different periodicities [70]; (b) polydomain [91]. S, B and I in (a) denote SrTiO₃, BaTiO₃ and interface layers respectively. Reprinted with permission from Ref. [70] (panel a), and Ref. [91] (panel b).

the polarization is mandatorily accompanied by the switching of one of the AFD order parameters. In magnetic materials, where magnetism arises from the superexchange interaction through the oxygens, such strong coupling between polarization and oxygen octahedron rotations is therefore a promising way of generating novel magnetoelectric couplings [11]. Ruddlesden–Popper compounds like Ca₃Mn₂O₇ have been recently proposed as possible candidates for realizing electric switching of the magnetization through so-called “hybrid” improper ferroelectricity [7, 53], with the ferroelectric order parameter triggered by an effective field generated by the rotation of the oxygen octahedra.

8 Conclusion and perspectives

Driven in part by the industrial needs for device miniaturization and in part by purely academic curiosity, the study of ferroelectrics is booming at the nanoscale. Materials processing as well as characterization techniques have finally reached the maturity that allows us to experimentally probe fundamental sized effects rather than those imposed by processing limitations. Along with the experimental advances, one of the most significant milestones in the study of ferroelectricity has been the development of powerful first principles calculations. Not only have these shed enormous light on the fundamental origin of ferroelectricity, but they are also an ideal way for describing experimental findings and for understanding the nature of ferroelectric size effects.

In this chapter, we have summarized some of the recent developments in the theoretical and experimental understanding of ultrathin ferroelectrics. Many aspects of thin film ferroelectrics are dictated by the depolarization field and the way in which the material tries to minimize it. The fundamental discovery that, with proper management of the depolarization fields, there seems to be no intrinsic size limitations to ferroelectricity, has important implications for technological applications, promising further downscaling of existing devices and opening doors to new devices based on ultrathin ferroelectrics. Studies of

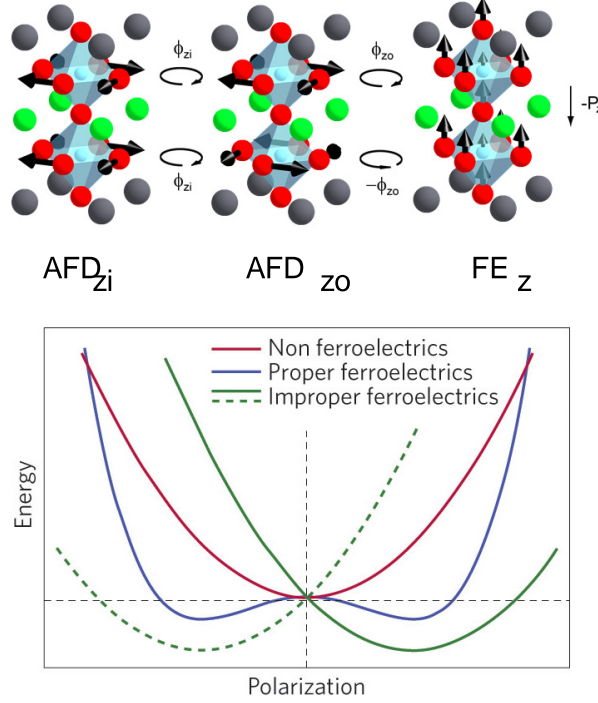


Figure 8: At the interface between PbTiO_3 and SrTiO_3 , the phase transition is driven by the two antiferrodistortive modes that correspond to in-phase (AFD_{zi}) and out-of-phase (AFD_{zo}) rotations of the oxygen octahedra and induce the polar distortion (P_z). The bottom panel illustrates, more generally, how a ferroelectric state can be induced in a non-ferroelectric material by either renormalizing the curvature of the free energy to produce a double well (e.g. by epitaxial strain) or by coupling to primary non-polar mode(s) inducing (hybrid) improper ferroelectricity [53]. Reprinted with permission from Ref. [53].

nanoscale domains and polarization vortices, as well as the properties of domain walls, have also been generating significant excitement, from both the theoretical and experimental communities, with many questions remaining unresolved and theoretical predictions to be confirmed. An increasing amount of research is being focused on heterostructures involving ferroelectrics or materials that combine ferroelectricity with other interesting properties. Today, there is tremendous excitement about the possibility of combining (and coupling) ferroelectricity and magnetism within a single multiferroic (magnetoelectric) compound or composite, yielding truly multifunctional materials, novel device ideas and fascinating new physics.

These recent experimental and theoretical developments also extend to the larger family of functional oxides, and fundamental research on this field, both on bulk phases and on complex oxides heterostructures, is living a momentous stage. The driving force that fuels these efforts is based on the fact that, within a relatively simple structure, these materials display a huge variety of properties that are susceptible to be used in electronic devices, including high- T_c

superconductivity (with critical temperatures far higher than in standard superconductors), colossal magnetoresistance (where the application of magnetic fields of a few teslas changes the electrical resistivity by orders of magnitude), ferroelectricity, magnetic ordering or even multiferroic behaviour. These properties are the result of a subtle interplay between different degrees of freedom, that include spin, charge, and orbital ordering. Very interestingly, the energy scales of these interactions are of the same order of magnitude, so a delicate balance between all of them is always present. Small changes on the condition might incline the balance towards one of the multiple local minima displayed in the energy landscape, yielding to very different ground states.

If already at the bulk level the physics of perovskite oxides is fascinating, the combination of different materials to form superlattices and complex oxide interfaces has opened new and unexpected research avenues. The behaviour of these heterostructures is far from being a linear combination of the properties of the two materials, as we've seen in the discussion of ferroelectric superlattices. Going beyond ferroelectric materials, the number of possible combinations is infinite, and completely exotic behaviours have already been observed, including metallic states at the interface between insulating materials or the appearance of improper ferroelectricity, with the ferroelectric order parameter triggered by an effective field generated by the rotation of the oxygen octahedra. Besides, the superlattices offer a powerful method for engineering and tuning desired properties by playing with the possible material combinations, periodicity of the structure, the strain or the electrical boundary conditions.

With these new properties we can easily envisage some dream come true, for instance, magnetically readable and electrically writable multiferroic devices, or systems with greatly enhanced thermoelectric properties for energy harvesting.

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